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(54) Title: **ELECTROCHEMICAL SENSOR SYSTEM AND SENSING METHOD**

(57) Abstract: A sensor system and method for measuring the concentration, or indicating the presence or presence at a predetermined level of, a target contaminant species in an aqueous medium are described. The system is based upon a sensor element having a sample receiving area for receiving a sample of aqueous medium to be sampled and which comprises at least three electrodes each comprising a layer of conductor deposited upon an insulating substrate. The system also includes a power source to apply a pre-determined potential difference across two of the electrodes determined by the potential associated with an electrochemical reaction characteristic of the target species, and output means to output data corresponding to the current generated thereby when a sample is in place on the sampling area.

ELECTROCHEMICAL SENSOR SYSTEM AND SENSING METHOD

The invention relates to a sensor system for the identification and/or
5 measurement of levels of target species in aqueous solution, and in particular
for the identification and/or determination of levels of contaminant species
such as nutrient species in the aqueous phase.

The invention is particularly directed to the provision of such a sensor system
10 in portable/hand-held and convenient form and/or adapted for use for the
identification and/or measurement of levels of target species in water in a real
(i.e. non-laboratory) and in particular external environment. The invention
also relates to a method for the identification and/or determination of levels of
target species in aqueous solution.

15 Sensors already exist for the determination of the presence of contaminant
species in water, in particular nutrient and related species such as ammonia,
ammonium, nitrates, nitrites and other ions, which are found in natural and
industrial water.

20 The measurement of these species at the low concentrations that may be
present in aqueous fluids is very important in a number of areas, including

- a) High purity boiler feed water supplies for power stations.
- 25 b) Drinking water production and maintenance of purity of supplies,
including untreated and treated river waters for water extraction.
- c) Waste water and sewage treatment processes.
- d) Steel work effluents and other trade water wastes.

- e) The agricultural industry has strong requirements to measure levels of ammonia/ammonium ion and like contaminants. Here salt rich fertilisers and their resultant leaching into water bodies are a concern.
- f) Furthermore even animal slurries and routes of disposal are sources where ammonia/ammonium ion and like contaminants are present.
- 5 g) In the food industry analysis of beer, wine, milk and meat products is carried out for ammonia/ammonium ion concentration levels.
- h) Clinical analysis in the medical world relies upon ammonia/ammonium ion measurements when considering liver and kidney efficiencies in particular urea and urine relationships. Even levels as low as 5 mg ammonia per 100 ml of blood are toxic to humans.

Existing basic devices often employ potentiometric principles where a potential only is measured. The output from the ion selective electrode (ISE) is indirectly related to the log of the concentration of the species of interest, in the water sample. A common example of an ISE is a glass pH electrode. These glass and other types of ion exchange membrane electrodes are readily available from a number of suppliers at costs often several hundred pounds. However, ISEs in general have well known problems and limitations, such as poisoning and restrictions of use in certain environments.

Ion exchange membrane plastic type electrodes suffer badly from the effects of debris in the aqueous sample, surfactants, particulate material, etc., can cause deterioration of the sensors performance. ISE electrodes whatever the type and nature of the membrane must therefore be routinely cleaned, ideally after each measurement.

Calibration of all ISEs is also a time consuming and costly procedure. The procedure requires at the very least a minimum of laboratory training so that

the electrode and measured value obtained can be relied upon. Hence care and a fair degree of scientific skill are necessary to ensure satisfactory operation.

5 A most important limitation of the present sensor technology is the inability of such sensors to be used directly in waters which have high levels of salinity. Corrections and further preparations for the measurement technique are required. Their instant use is therefore excluded from waters in this category which may be estuarine, or coastal, without substantial preparation of the sample. These factors are a significant drawback to their general use.

10

Other well known methods for analysis of ammonia/ammonium ion and other water contaminant species also exist using various 'wet' chemical techniques often relying upon a colour change or similar. These methods require even more of a degree of technical skill and experience to be used successfully than
15 the ISE electrode technology discussed above. Additionally these wet methods are prone to interference from the strong oxidising or reducing agents or complexing species found in the water samples. Well known wet methods require a sample to be taken to the laboratory for measurement with suitable bench type equipment, e.g., ion chromatography, Kjeldahl apparatus, etc.,
20 However, these types of measurements are often accepted as standard, but require time, effort, and technical data interpretation problems by qualified staff.

Thus to overcome these particular problems considerable time and effort is
25 required for sample preparation and pre-treatment.

It is also generally the case that the ability of existing analysis measurement systems for ammonia/ammonium ion and other target species to give data

immediately or in-situ with ease and reliability in seawater and brackish waters is limited.

It is an object of the invention to provide an in-situ use sensor system and method that also mitigates some or all of the above disadvantages in relation to the monitoring of the concentration, or presence, or presence at a predetermined level of a target water contaminant and in particular a nutrient species such as ammonia/ammonium ion, nitrate, nitrite, etc.,

10 It is a particular object of the invention to provide a sensor system and method that employs established electrochemical principles in a manner that is reliable, cost effective and user friendly.

It is a particular object of the invention to provide a sensor system and method that lends itself to use in in-situ site use in the field and/or by relatively untrained personal.

Thus, according to the invention in a first aspect, a sensor system for measuring the concentration, or indicating the presence or presence at a predetermined level of, a target contaminant species in an aqueous medium comprises a sensor element having a sample receiving area for receiving a sample of aqueous medium to be sampled and which comprises at least three electrodes each comprising a layer of conductor deposited upon an insulating substrate, and further comprising a power source adapted to apply a predetermined potential difference across two of the electrodes determined by the potential associated with an electrochemical reaction characteristic of the target species, and output means to output data corresponding to the current generated thereby when a sample is in place on the sampling area.

The active part of the sensor system thus comprises three active small mutually insulated electrode sites in the sample collection area and contacting the aqueous sample in use. The general principles of chemistry underlying the operation of the sensor system in this active area will be known. The power
5 source is connected to the sensor system to create a sensor system control circuit which can effectively function as a potentiostat.

Sensor system sensitivity performance can be improved by use of other well-known circuits producing cyclic voltammetry measurements or better
10 differential square wave pulsed techniques. The latter could easily replace the constant potential amperometry described in this patent.

Two electrodes are polarised in the sample collection area at a pre-determined particular potential characteristic of an electrochemical reaction (E^0)
15 indicative of the species under investigation. Polarising the electrodes results in generation of a current as the electrochemical reaction involving the target species proceeds, and this quite rapidly settles into a steady change state where the current is proportional to the concentration of the target species. One of the electrodes is used to provide a reference point so that the working
20 electrode can be set at a specific potential. The third electrode, the counter, completes the circuit.

The applied voltage, which is carefully selected to carry out the specific and unique process or reaction in the sensor cell, results ultimately in the
25 generation of an electric current. This current is directly related to the process being carried out at the sensor cell and is either an oxidation or reduction process at the working electrode.

Although the system employs known and established electrochemical principles, the sensor is greatly simplified over many prior art systems, which employ large-scale electrodes and/or which employ potentiometric principles where a potential difference is measured. In particular it will be seen, the
5 sensor is in effect pre-calibrated and provided with an integral reference electrode. There is no need for calibration in the field. The first sample of liquid on the sample receiving surface produces a potential change. This goes to a pseudo steady state in a relatively short time.

- 10 The system requires only a small sample of liquid to function effectively. For example a single drop or a few such drops of liquid to be tested may be applied to the sample receiving area. Larger quantities of sample may be used. For example the sensor may be partly or completely immersed into a liquid to be tested such that a sample contacts the sample receiving area, either
15 by direct immersion in situ or, more conveniently, by immersion of the sensor in a quantity of collected sample in a suitable container.

- The electrodes acting in this manner are small, cheap and in a preferred embodiment are intended to be disposable. Because of the accurate control of
20 properties of the electrodes which is possible by using conductor layer on insulating substrate technology, for example thick or thin film conductor technology, in particular with noble metals of very high purity, separate sensor electrode elements do not need to be separately calibrated. Purity of the metal deposited is crucial and highly important in obtaining acceptable repeatability.
25 For a given material and electrode configuration combination the behaviour of the electrodes varies to a sufficiently small extent, when using very pure metal, to render this unnecessary. Consequently the sensor system is self referencing, and is therefore very easy to use in real environmental situations in the field to a reasonable level of accuracy.

A strong advantage of the present invention is in its ability to be used quickly for in-situ/in-field type measurements. In this respect an advantage by comparison with other methods that require collection of a sample and taking
5 it back to a laboratory for analysis. Alternatively, and at best, pre-treating the sample on site and obtaining indifferent data from the method employed in its measurement.

In operation, a few millilitres, of solution is taken from the bulk sample, which
10 might be a river, an ocean or simply a glass of water. This is placed for testing on the sample collection area.

To this sample may be added a pH buffering agent. This buffering agent is a preferably non-toxic chemical reagent, which will adjust the pH of the sample
15 to a value acceptable and necessary for the characteristic electrochemical process to be tested. For example a buffering agent is selected to vary the pH of the initial solution to free into solution a species related to and indicative of the contaminant species under test, the characteristic electrochemical process to be tested by the sensor being one involving this related species.

20

In an example, when testing for ammonia/ammonium ion, a solution of interest would have a buffer added, changing the pH of the test solution to about pH 11 to 12. At this alkaline pH value, and with the application of a suitable and specific voltage, free liberated ammonia present in the sample is
25 oxidised, by the current producing electrochemical process

Additionally or alternatively to this sample may be added a standard reference reagent, that is a reagent which sets up a suitable standard reference cell in situ involving the reference electrode to provide a reference for the working

electrode. For example, suitable for target species such as ammonia/ammonium ion, then sodium chloride is added to a suitable standard solution concentration, for example at a concentration of around 30 g l^{-1} , to the solution. That is part of the standard solution described which, in conjunction
5 with the silver reference electrode, will set up a standard Ag/AgCl reference in situ on the device.

In the measurement process only a small volume of sample is required, hence only a small quantity of buffering reagent is required to adjust the sample pH
10 to a desired level irrespective of the original pH of the sample solution source. Equally, only a small quantity of standard reference reagent is required to adjust concentration levels in the sample to reference levels and this is again largely irrespective of the original level in the sample solution source. Both of these might vary between, for example, seawater, drinking water, and treated
15 sewage effluents. Hence the process is straightforward and achievable with little cost, and effective regardless of the sample solution source.

A number of advantages will be apparent over prior art systems.

20 First, the electrode units are inexpensive to manufacture, allowing a measurement to be made by the user at little cost. It is practical for the electrodes to be intended for disposable single use. The sensor is not manufactured from glass and is therefore less fragile.

25 Second, the sensor system is simple to use. In a preferred embodiment it can be fabricated as a "black box" comprising, in compact operative association, a holder for a removable and optionally disposable electrode, a power source, an output means, access to the sample collection area when an electrode is inserted, and an actuator to initiate measurement, and optionally further a

readily user readable display. Thus a user merely needs to insert an electrode, add of a drop of water, and press a button to initiate the measurement process. Hence there is no need or requirement for a highly trained or skilled operator.

- 5 Third, the measurement process is quick, requiring only one or two minutes or so before a subsequent measurement result is displayed. The measurement method is both safe and environmentally friendly, an important advantage over some existing methods. In practice the conditioning reagents do not require separate preparation (c.f. ISE system for example where a calibration
10 is necessary then followed by reagent treatment of sample for measurement, etc.). With the sensor system all the necessary steps are obtained when the sample is put in contact with the electrode assembly.

- An added and significant advance over the current methods of analysis
15 generally available is that the sensor is largely unaffected by chemical materials commonly found in the aqueous environment. Debris will not influence the measurement process. Other ionic species present in the sample have been shown not to affect the sensor's performance. Deterioration of the sensor with time and routine use will not be a concern because of the intended
20 protocol of operation. There is an ability to make measurements in aqueous samples that possess high levels of salinity. This will potentially allow measurements in estuarine waters, where salinity changes, or even in the sea and oceans where high levels of salinity are found. This is an important area where conventional ISE electrodes fail, or require special consideration of
25 preparation. There are also areas in the medical world where an ammonia/ammonium ion sensor capable of use in a saline solution would be advantageous, e.g., blood, and urine analysis.

The power source causes the sensor system circuit to function as a potentiostat. To gain great sensitivity and repeatability, a variant of the simple potentiostatic circuit, that of a differential pulsed square wave voltammetric circuit could be used, and suitable control means are provided in the power
5 source to effect this.

The power source may be any suitable electrical power source, and is preferably portable for use in the field, and for example comprises a battery, for example remotely rechargeable, a fuel cell, optionally disposable, or the
10 like.

The output means deals with a primary output of a quasi steady state current, and comprises processing means to output this as unit readable data corresponding to this current in any suitable form. For example unit readable
15 data may be suitable for output to any suitable display means and/or any suitable data register in data storage and/or processing means such as a computer. The output means might be adapted such that the data may correspond to measured current, which can then be compared to a reference database to produce useful data indicative of the concentration and/or presence
20 and/or presence at a predetermined level of the target species in the solution under test.

Additionally or alternatively the output means may be associated with conversion circuitry to convert the primary output, for example by comparison
25 to pre-recorded reference data, to secondary output comprising unit readable data directly indicative of the concentration and/or presence and/or presence at a predetermined level of the target species in the solution under test.